# PROBLEMS OF QUALITY

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## IDENTIFICATION OF QUALITY PARAMETERS FOR BARIUM TITANATE POWDER

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The authors describe the results of developing methods for determining some quality parameters of barium titanate powder, which is the main component in some ceramics that are used to produce capacitors. The degree of transformation of ZnO and $BaTiO_3$, the volume density of sintered powder, the degree of its dissolution in hydrochloric acid, and some diffraction characteristics of $BaTiO_3$ powders are determined according to the developed methods and can predict with a sufficient degree of reliability the quality of ceramic capacitors made from barium titanate powders.

The progress of microelectronics has caused a sharp increase in the production of ceramic capacitors. The majority (around 90%) of those are low-voltage fixed capacitors, among which the most common are disk and plate single-layer capacitors, as well as multilayer continuous ones.

The wide application of ceramic capacitors is due to several advantages, such as implementation of a wide range of capacities, temperature stability of capacity, high dielectric permeability, reliability and operability in various conditions, and simplicity of design [1].

The production of ceramic capacitors involves many technological operations and at the electric parameters of the finished product may be impaired in any operation. Furthermore, the quality of capacitors depend on the composition of the initial mixture of oxide metal compounds, their capacity for single-phase reactions [2, 3], and the conditions of sintering of emerging multicomponent solid solution particles.

The main component in numerous ceramic materials used to produce capacitors is barium titanate $BaTiO_3$. Therefore, it can be assumed that in some cases defects in the finished products are due to the poor quality of $BaTiO_3$ powder.

Powdered $BaTiO_3$ is characterized by the following parameters [4]: bulk weight, molar ratio $BaO : TiO_2$, content of "free" barium oxide, quantity of residue insoluble in hydrochloric acid, content of impurities, and specific surface area. The residue insoluble in HCl is indirect evidence of the content of insoluble polytitanates which degrade the batch sintering process and electric characteristics of the finished product. Experience shows that $BaTiO_3$ powder with satisfactory specified characteristics does not always yield products of good quality with required parameters.

In this context it has become necessary to develop methods for identifying additional quality parameters of $BaTiO_3$ powder. The present paper is dedicated to solving this problem. We investigated various batches of $BaTiO_3$ powder. Powders that yield capacitors with the required parameters are arbitrarily called "positive" and powders that yield poor-quality capacitors are called "negative."

It is known that the course of many reactions with participation of polycrystalline solid compounds depends on their chemical activity [2 – 4], which, in turn, depends on many factors: crystal lattice defects, polydispersion, presence of impurities, etc.

Our goal was to study solid-phase reactions with the participation of barium titanate, and its dissolution and sinterability, in order to obtain additional quality characteristics of $BaTiO_3$ powders. Of numerous solid-phase reactions with participation of $BaTiO_3$ [5 – 7], we chose for detailed study its reaction with ZnO contained in the initial mixture, since the latter is added to the mixture to improve the sinterability of the system components and to obtain capacitors with preset Curie point and dielectric permeability.

An equimolar mixture of $BaTiO_3$ and ZnO was thoroughly ground in an agate mortar; then some ethyl alcohol was added to it and tablets were molded. The tablets were dried for 1.5 h at a temperature of 400 K and then annealed at the temperature of 1373 K for 2 h. After cooling, the tablets

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**TABLE 1**

| "Positive" powders | | "Negative" powders | |
|---|---|---|---|
| powder | α, % | powder | α, % |
| 1 | 10.8 | 5 | 1.8 |
| 2 | 7.2 | 6 | 2.4 |
| 3 | 6.8 | 7 | 1.6 |
| 4 | 9.0 | 8 | 1.2 |

were ground in the agate mortar and the powder was analyzed for its content of free ZnO (which had not reacted).

To determine the content of free ZnO, a portion of powder was dissolved in a mixture containing 15% solution of $NH_4Cl$ and ammonia solution (1 : 1) at a temperature of 343 K for 20 min. The insoluble residue was filtered and thoroughly rinsed, and the rinse water was added to the filtrate. To identify the quantity of $Zn^{2+}$ ions contained in the filtrate we used the comlexonometric method [8], according to which the filtrate was titrated with Trilon B solution in the presence of xylenol orange indicator at pH = 5.5. The final result of the analysis was the quantity of free zinc oxide $n$ (mole) in batch samples after sintering. The quantity of ZnO in the initial samples $n_0$ was known from the conditions of the experiment.

The reactivity of $BaTiO_3$ powder was estimated based on the degree of transformation of ZnO:

$$\alpha = \frac{n_0 - n}{n_0} \times 100\ \%.$$

The degree of transformation of ZnO in sintering mixtures of $BaTiO_3$ and ZnO is given in Table 1.

It can be seen that powders 1 – 4 more intensely react with ZnO than powders 5 – 8. This suggests that the sinterability of powders 1 – 4 should be better as well. Consequently, we investigated the process of isothermic sintering of powders $BaTiO_3$ and determined the volume density of sintered samples.

Sintering samples were molded as tablets and placed in a platinum container. To prevent surface contact, the tablets were separated from each other by platinum plates. The container was placed in a quartz tube after it acquired the temperature of the furnace. The temperature was measured by a platinum/platinum-rhodium thermocouple. The annealing lasted 2 – 10 h at the temperature of 1573 K. To determine the volume density of sintered samples, the geometric sizes of the tablets were determined using a MKO-25 micrometer. All calculations were based on mean values found from ten measurements. The weight of the tablets was determined on an analytical scale with an accuracy of ± 0.0001 g. The volume density was calculated from the following formula:

$$\rho = \frac{m}{V},$$

where $m$ is the tablet weight, g; $V$ is the tablet volume, $cm^3$.

The volume density data are listed in Table 2.

**TABLE 2**

| Duration, h | Volume density, $g/cm^3$, of powders | | | |
|---|---|---|---|---|
| | "positive" | | "negative" | |
| | 1 | 2 | 5 | 6 |
| 2 | 4.635 | 4.316 | 3.933 | 4.007 |
| 3 | 4.752 | 4.405 | 3.985 | 4.015 |
| 4 | 4.837 | 4.425 | 4.014 | 4.019 |
| 10 | 4.871 | 4.480 | 4.045 | 4.021 |

It can be seen from Table 2 that barium titanate powders 1 and 2 sinter better than samples 5 and 6 and have a higher volume density.

The results obtained in studying the extent of interaction between the components of the mixture of $BaTiO_3$ and ZnO and the sinterability of $BaTiO_3$ powders agree for each group of samples. Therefore, the degree of transformation of ZnO in the mixture of $BaTiO_3$ and ZnO and the volume density of barium titanate after sintering can be used as quality parameters of powders $BaTiO_3$.

One can also estimate the quality of $BaTiO_3$ powder based on the duration of its dissolution in an acid or a mixture of acids, as well as the extent of its dissolution within a certain time lapse [4]. The degree of dissolution of $BaTiO_3$ powder can be monitored by different physicochemical methods. We chose the colorimetric method which makes it possible to determine the concentration of barium titanate that has dissolved based on the optical density of the solution, provided that titanium cations in the solution acquire a tinted form. The peroxide method satisfies these requirements [8]. The point of this method is as follows. Titanium in acid solutions usually exists in the form of $TiO^{2+}$ ions. After hydrogen peroxide is added to this colorless solution, a complex cation $[TiO \cdot H_2O]^{2+}$ is formed, which tints the solution yellow. Since the solution color intensity correlated with the content of $TiO^{2+}$, the optical density parameter can be used to estimate the quantity of $BaTiO_3$ that dissolves into the solution.

After preliminary experiments intended to select a solvent and conditions for dissolving $BaTiO_3$ powder it was found that the dissolution proceeds at the optimal rate at a temperature of 313 K in 4 M solution of HCl.

The experiments in determining the degree of dissolution of $BaTiO_3$ powder in HCl were performed according to the following schedule. A round-bottom flask with 4 M solution of HCl and a portion of $BaTiO_3$ powder in a Teflon cup were placed into a thermostat and after reaching a constant temperature of 313 K the sample was dissolved for 5 min under intense stirring. Next, the flask with its content was placed in cold water to delay the dissolution of $BaTiO_3$. The residue was filtered and the filtrate was subjected to colorimetry.

The determination of optical density $D$ was performed using a photoelectrocolorimeter with a wavelength of 400 nm in a cuvette of thickness 0.505 cm. The obtained data

**TABLE 3**

| "Positive" powders | | "Negative" powders | |
|---|---|---|---|
| powder | *D* | powder | *D* |
| 1 | 0.35 | 5 | 0.47 |
| 2 | 0.32 | 6 | 0.52 |
| 3 | 0.30 | 7 | 0.49 |
| 4 | 0.29 | 8 | 0.45 |

**TABLE 4**

| "Positive" powders | | "Negative" powders | |
|---|---|---|---|
| powder | *b*, mm | powder | *b*, mm |
| 1 | 6.8 | 5 | 10.1 |
| 2 | 7.0 | 6 | 9.2 |
| 3 | 6.9 | 7 | 10.2 |
| 4 | 7.1 | 8 | 10.0 |

are given in Table 3. It can be seen that the optical density of the "positive" powder solutions is lower than that of the "negative" ones. Consequently, one can speak of a correlation between the powder quality and the parameter *D*.

Thus, the optical density of such solutions can be used to characterize the quality of $BaTiO_3$ powders.

To find additional quality parameters for $BaTiO_3$ powders we also used x-ray phase analysis. The diffraction patterns of both "positive" and "negative" powders were recorded at room temperature by a DRON-3 diffractometer ($CuK_\alpha$ radiation, Ni filter). Diffraction patterns in the first series of experiments were registered in the interval 2θ from 10 to 80°. The rotational speed of the counter was over 1 deg/min. The diffraction patterns of positive and negative powders were virtually identical, and no significant difference was registered. More interesting data were obtained from diffraction patterns taken in the interval 2θ from 139 to 143°. The rotational speed of the counter was over 0.5 deg/min. It was found that the width *b* of the diffraction maximum 2θ = 141.25° at a distance of 1/3 peak height from the peak vertex is different for "positive" and "negative" powders (Table 4). It can be seen that the peak width of the "positive" powders is smaller than that of "negative" powders. Consequently, it is possible to speak of a correlation between the quality of $BaTiO_3$ powder and the parameter *b*.

Based on the performed studies, one can evaluate the quality of $BaTio_3$ powders used to produce capacitors and other products. It was found that of all powders considered (altogether eight samples), only two samples can be classified as "negative" according to the proposed qualities parameters, whereas the rest can be considered "positive."

In order to verify the reliability of the prediction of $BaTo_3$ powder quality, capacitors were made of these powders and their electrophysical properties were determined [1]: resistivity, capacity, temperature stability of capacity, dielectric permeability, dielectric loss tangent, and Curie point.

The analysis of the electrophysical parameters of finished products established that unsatisfactory capacitors were produced from both "negative" powders and from one "positive" powder (sample 6).

Thus, the reliability of the prediction of capacitor quality can be regarded as quite acceptable. The proposed procedures can be used to determine additional quality parameters of barium titanate powder, which is the basis for producing capacitors.

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